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HCl Vapour Pressures and Reaction Probabilities for ClONO₂ + HCl on Liquid H₂SO₄–HNO₃–HCl–H₂O Solutions

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Henry's Law solubility constants for HCl have been measured for liquid H₂SO₄–HNO₃–HCl–H₂O solutions; the results are in good agreement with predictions from published semiempirical models. The ClONO₂ + HCl reaction on the surfaces of such solutions with compositions simulating those of stratospheric aerosols has been investigated; as the composition changes following the temperature drop characteristic of the high-latitude stratosphere the reaction probability γ increases rapidly. Furthermore, the γ values remain essentially unchanged when HNO₃ uptake is neglected; the controlling factor appears to be the solubility of HCl. These results corroborate our earlier suggestion that supercooled liquid sulfate aerosols promote chlorine activation at low temperatures as efficiently as solid polar stratospheric cloud particles.

The importance of heterogeneous reactions involving ClONO₂, HCl, N₂O₅ and H₂O on the surfaces of polar stratospheric cloud (PSC) particles has been well established in connection with the observation of large-scale ozone depletion during the Antarctic springtime.^{1,2} Laboratory studies have shown that both solid and liquid particles can promote heterogeneous reactions such as the following, converting the relatively inert chlorine reservoir molecules (ClONO₂ and HCl) into species (Cl₂, HOCl) which are readily photolysed to yield chlorine radicals:



In particular, heterogeneous reactions on sulfuric acid aerosols have recently been under intense study since these particles may play a role in mid-latitude ozone depletion.^{3–6} Hanson *et al.*⁷ have described a framework for applying the results of these experimental studies to the modelling of the actual micrometre sized liquid sulfuric acid aerosols found in the stratosphere. It was concluded in these studies that reactions (1)–(3) become important at sulfate aerosol compositions corresponding to low atmospheric temperatures ($T < 200$ K), in agreement with our earlier suggestion that stratospheric aerosol particles need not freeze in order for chlorine activation reactions to proceed efficiently at high latitudes.⁸

It is important to determine accurately the composition of the aerosols as a function of the temperature and partial pressures of their constituents in order to model the various possible heterogeneous reactions adequately. Several groups have investigated uptake of HNO₃⁹ and HCl^{4,10,11} by sulfuric acid solutions. Vapour pressures of these constituents dissolved in bulk solutions have also been measured.¹² In addition, some of this data has been used to construct semi-empirical thermodynamic models which are

intended to predict sulfate aerosol composition.^{13,14} Although it has been shown that HNO_3 and HCl uptake by stratospheric sulfate aerosols is negligible for equilibrium temperatures above 210 K, the solubility of these species increases rapidly with decreasing temperature. Field observations of total aerosol volume at high northern latitudes have commonly been interpreted as evidence for solid PSC formation, since the aerosol volume is observed to rise quickly over a temperature range near the nitric acid trihydrate (NAT) frost point.¹⁵ However, these observations are more consistent with the existence of supercooled liquid sulfate aerosols with substantial nitric acid content than with the existence of solid PSC particles.¹⁶

Since the reaction probability for the $\text{ClONO}_2 + \text{HCl}$ reaction depends very sensitively on the HCl concentration in the aerosol, it is particularly important to determine accurately the solubility of HCl in solutions with compositions of atmospheric relevance. The existing results for the HCl solubility in sulfuric acid solutions are in conflict; in particular, the Henry's Law coefficients determined earlier in our laboratory¹² deviate significantly from similarly extensive measurements of Hanson and Ravishankara⁴ and from the thermodynamic model predictions of Luo *et al.*¹³

Here we describe further measurements designed to resolve the discrepancy in the solubility results for the ternary $\text{H}_2\text{SO}_4\text{--H}_2\text{O--HCl}$ system, and report the first measurements of Henry's Law coefficients for HCl for the quaternary ($\text{H}_2\text{SO}_4\text{--HNO}_3\text{--H}_2\text{O--HCl}$) system. We also report measurements of $\text{ClONO}_2 + \text{HCl}$ reaction probabilities on the surface of such ternary and quaternary supercooled solutions with compositions relevant to the stratosphere.

Experimental

The HCl vapour pressures and the reaction probabilities for the $\text{ClONO}_2 + \text{HCl}$ reaction were measured using a vertical wetted-wall flow tube coupled to a differentially pumped molecular-beam-sampling quadrupole mass spectrometer. The vertical flow tube is similar to that employed by Utter *et al.*¹⁷ for measurements of ozone uptake on aqueous surfaces.

The top of the vertically aligned flow tube (id 2.4 cm) was fitted with a liquid delivery system that contained inlets for the helium carrier gas, a movable injector and the sulfuric acid solution. The delivery system consisted of an annular cup which, when filled with liquid, overflows to create a falling cylindrical film of acid on the inner wall of the flow tube. This wetted-wall technique has been widely used in the field of chemical engineering, and Danckwerts¹⁸ has described the fluid dynamics of such flow. In order to maintain cold, stable temperatures, it was necessary to shut off the acid solution flow during actual measurement of HCl vapour pressures. The temperature of the acid was assumed to be the temperature of the coolant (which was sampled at the inlet to the flow tube) when the HCl signal was observed to stabilize (of the order of a few minutes). The flow-tube wall was rinsed with fresh solution for each measurement in order to minimize the possible effects of dehydration: there is insignificant dehydration of such acid solutions on such short timescales, as shown by Hanson and Ravishankara.¹⁹ The carrier gas was sampled at the end of the flow tube and directed to the detection system, while the slowly moving acid film was collected in a bulb maintained at temperatures below that of the flow tube in order to prevent backstreaming of the vapours.

Most measurements were made with flow tube pressures of *ca.* 1 Torr and carrier gas flow velocities of *ca.* 1000 cm s^{-1} . The saturation of the carrier gas with HCl vapour was checked by directing the helium flow through the moveable injector; the observed HCl signal did not change with injector position, thus confirming the equilibrium condition. In order to determine absolute values for the HCl vapour pressures, the mass spectrometer was calibrated using the extrapolated $\text{HCl--H}_2\text{O}$ data of Fritz and Fuget.²⁰ The detection limit for HCl (monitored at mass 36) using these methods was *ca.* 10^{-7} Torr.

ClONO_2 partial pressures of $\text{ca. } 10^{-6}$ Torr were used for the kinetics measurements and the possible reactive depletion of HCl was investigated for each solution. Because the electron-impact ionization scheme results in the production of NO_2^+ for both ClONO_2 and HNO_3 , it was necessary to detect the reaction product, Cl_2 , for the quaternary solutions (since the ambient HNO_3 vapour pressures were high enough to interfere with the ClONO_2 signals). Reaction probabilities were determined using standard cylindrical flow tube analysis techniques.²¹

Bulk solutions were prepared by diluting 96% H_2SO_4 , 70% HNO_3 and 37% HCl with deionized water. The solutions were spot-checked for composition with density and standard acid-base titration measurements.

Results and Discussion

HCl Vapour Pressures

Henry's law solubility constants for HCl were determined for two ternary solutions and for two quaternary solutions over a range of temperatures (*ca.* 205–235 K) of stratospheric relevance. A 50% H_2SO_4 ternary solution was chosen for study to allow direct comparison with previous measurements. The other solutions were chosen in order to test the thermodynamic model of Luo *et al.*¹³ for compositions of atmospheric interest. Neglecting uptake of HNO_3 , it may be inferred that at a stratospheric temperature of *ca.* 190 K at 50 mbar the aerosols will contain 43% H_2SO_4 by weight, assuming 5 ppm by volume H_2O . We therefore measured solubility constants for this composition, for which the uptake of HCl is almost surely large enough for the $\text{ClONO}_2 + \text{HCl}$ reaction to be quite important. In order to spot-check the Luo *et al.* model further, we chose two quaternary solutions that correspond to aerosol compositions at equilibrium temperatures of 198 and 196 K at 100 mbar, with 10 ppb by volume HNO_3 and 2 ppb by volume HCl; these solutions contain significant levels of nitric acid (3.5% and 12.5%, respectively).

Table 1 contains the measured Henry's Law solubility constants (H^*) for the four solutions considered. In Fig. 1, the various results for the 50% H_2SO_4 solution are presented. In earlier work in our laboratory¹² the vapour pressure data was parametrized as a function of temperature, and it is shown in Fig. 1 as a dashed line. The results from the model of Luo *et al.*¹³ are shown as a solid line, and each data point from Hanson and Ravishankara,⁴ Williams and Golden,¹¹ and this work is shown individually. Our new results form a consensus with two of the previous measurements and with the model predictions, while the Zhang *et al.*¹² data lies well outside the range of the consensus findings. The reason for the discrepancy is not clear; it is most likely a consequence of HCl calibration errors in our earlier work. In Fig. 2, the H^* values for the 43% H_2SO_4 solution are plotted together with the model predictions of Luo *et al.*;¹³ as can be seen in the figure, the agreement is very good.

In Fig. 3, our measured HCl Henry's Law constants for the two quaternary solutions are presented together with the predictions from the thermodynamic model; once again, for these atmospherically relevant compositions, the agreement is excellent. These measurements are not intended to be an exhaustive test of the accuracy of the model; nevertheless, as has been shown to be the case for the ternary solutions it appears that the model also predicts the HCl solubility for quaternary systems very accurately.

Reaction Probabilities for $\text{HCl} + \text{ClONO}_2$

The compositions of the bulk solutions used for the kinetics investigations simulated those of typical stratospheric aerosols. These compositions were determined by using the Luo *et al.*¹³ model to search for mixtures whose vapour pressures correspond (within

Table 1 Experimental Henry's law solubility constants

composition	<i>T</i> /K	<i>H</i> [*] /mol dm ⁻³ atm ⁻¹
50% H ₂ SO ₄ 9.2 × 10 ³ mol dm ⁻³ HCl	225	4.0 × 10 ⁵
	222	5.2 × 10 ⁵
	219	7.2 × 10 ⁵
	216	9.8 × 10 ⁵
	214	1.2 × 10 ⁶
	211	1.8 × 10 ⁶
	208	2.3 × 10 ⁶
43% H ₂ SO ₄ 3.0 × 10 ⁻² mol dm ⁻³ HCl	226	2.5 × 10 ⁶
	222	4.1 × 10 ⁶
	218	6.8 × 10 ⁶
	214	9.2 × 10 ⁶
	208	1.8 × 10 ⁷
48% H ₂ SO ₄ 3.5% HNO ₃ 3.9 × 10 ⁻³ mol dm ⁻³ HCl	233	8.8 × 10 ⁴
	231	1.1 × 10 ⁵
	226	1.7 × 10 ⁵
	222	2.7 × 10 ⁵
	216	5.4 × 10 ⁵
36.2% H ₂ SO ₄ 12.5% HNO ₃ 6.2 × 10 ⁻³ mol dm ⁻³ HCl	228	5.5 × 10 ⁵
	223	1.2 × 10 ⁶
	218	1.7 × 10 ⁶
	213	2.8 × 10 ⁶
	208	4.7 × 10 ⁶

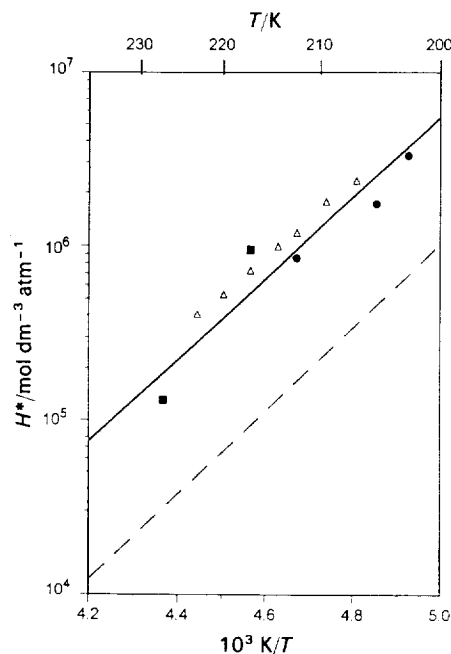


Fig. 1 Henry's Law constants as a function of temperature for a 50% H₂SO₄ solution. (— —) data from Zhang *et al.*,¹² and (—) from the semi-empirical model of Luo *et al.*¹³ △, our data, ■, data from Williams and Golden¹¹ and ●, from Hanson and Ravishankara.⁴

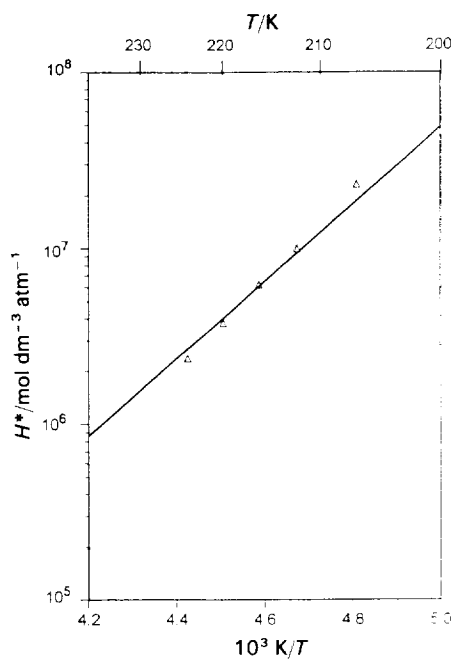


Fig. 2 Henry's Law constants as function of temperature for a 43% H_2SO_4 solution. The line represents estimates from the Luo *et al.* model¹³ and Δ , represent our data.

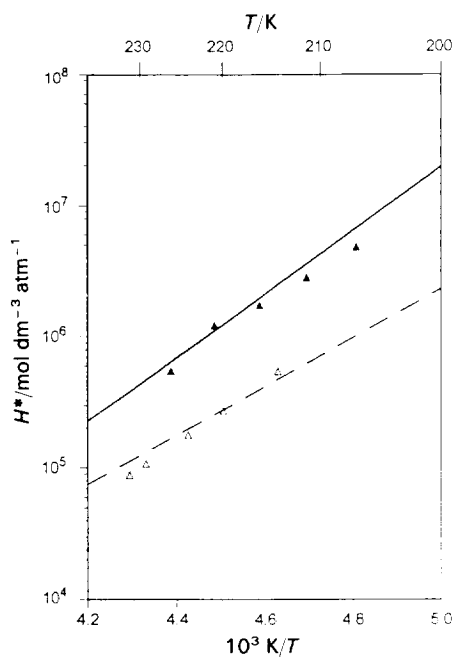


Fig. 3 Henry's law constants as function of temperature for the two quaternary solutions studied in this work. The lines represent estimates from the Luo *et al.* model¹³ and Δ , our data. (—) and \blacktriangle , 36.2% H_2SO_4 -12.5% HNO_3 solution, (---) and Δ , 48.0% H_2SO_4 -3.5% HNO_3 solution.

10%) to various atmospheric equilibrium temperatures $T(\text{eq})$, assuming 5 ppm by volume H₂O and 2 ppb by volume HCl at 100 mbar (*ca.* 16 km altitude), with no HNO₃ in Table 2 and 10 ppb by volume HNO₃ in Table 3. As the equilibrium temperature is lowered from 199 to 195 K, the weight fraction of HNO₃ in the solution increases from 2.2% to 28.3%, and the amount of HCl increases by more than a factor of 30. For aerosols at equilibrium with an atmosphere of 50 mbar total pressure and the same mixing ratios, similar compositional changes are expected at temperatures shifted by *ca.* 4 K below the 100 mbar values. We did not account for depletion of gas-phase HNO₃ or HCl in the calculation of the equilibrium compositions; it should not be significant for background aerosol sulfate loadings in the temperature range considered in this work.¹⁶ For ease of discussion, we will hereafter refer to each solution by its equilibrium temperature and by whether it contains nitric acid [*i.e.*, 197 K (no HNO₃)].

In Fig. 4 we present loss and production curves for ClONO₂ and Cl₂, respectively, for the 198 K (no HNO₃) solution; the two curves yield similar first-order rate constants. The reaction probability values (γ) for the two nitric acid scenarios are listed in Tables 2 and 3, and are the result of an average of at least three separate measurements. Through the use of bulk solutions prepared with specific compositions, we have effectively decoupled the atmospheric equilibrium temperature from the laboratory temperature; the former has a much larger effect on the reaction probabilities. Because of the tendency of the supercooled solutions to freeze, it was necessary to measure the reaction probabilities at laboratory temperatures which are higher than the atmospheric equilibrium temperatures. As shown in Table 4, the variation in the reaction probability for the 197 K (no HNO₃) solution over the laboratory temperature range 203–233 K was quite small, of the order of the experimental uncertainty. The 195 K (HNO₃) solution lies well within the nitric acid trihydrate (NAT) stability region of the phase diagram,⁸ and we were unable to cool the solution below 223 K without freezing. All other reaction probability measurements were carried out at 213 K and usually also at

Table 2 Reaction probabilities for the ternary H₂SO₄–H₂O–HCl system measured at 203 K, as a function of atmospheric equilibrium temperature

$T(\text{eq})/\text{K}$	weight fraction H ₂ SO ₄	weight fraction HCl	reaction probability
201	0.552	3.00×10^{-6}	0.010
199	0.520	1.60×10^{-5}	0.022
198	0.510	2.40×10^{-5}	0.038
197	0.490	6.00×10^{-5}	0.061
196	0.470	1.40×10^{-4}	0.083
195	0.450	3.44×10^{-4}	0.12
194	0.430	8.24×10^{-4}	0.30

Table 3 Reaction probabilities for the quaternary H₂SO₄–HNO₃–H₂O–HCl system measured at 203 K, as a function of atmospheric equilibrium temperature

$T(\text{eq})/\text{K}$	weight fraction H ₂ SO ₄	weight fraction HNO ₃	weight fraction HCl	reaction probability
199	0.503	0.022	1.38×10^{-5}	0.021
198	0.480	0.035	2.70×10^{-5}	0.026
197	0.440	0.061	6.18×10^{-5}	0.058
196	0.362	0.126	1.76×10^{-4}	0.070
195	0.202	0.283	4.88×10^{-4}	0.110

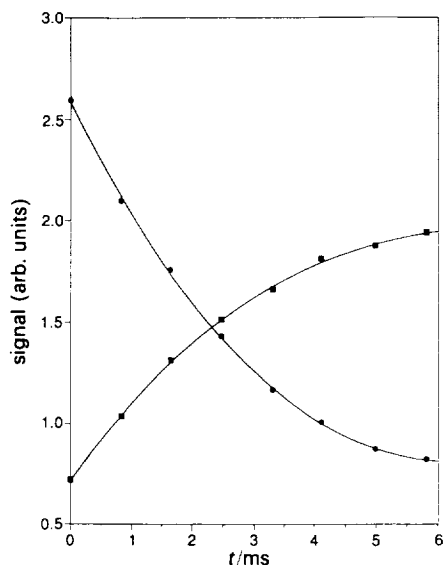


Fig. 4 ●, Loss (ClONO_2) ($k = 315 \text{ s}^{-1}$) and ■, production (Cl_2) ($k = 322 \text{ s}^{-1}$) curves for the $\text{HCl} + \text{ClONO}_2$ reaction on the 198 K (no HNO_3) solution measured at a laboratory temperature of 213 K

203 K, so that the extrapolation to the atmospheric temperature was not extreme. Hanson and Ravishankara⁵ had already noted that the reaction probability is nearly independent of temperature for solutions of a given composition; they attributed this behaviour to a fortuitous compensation of effects.

In Fig. 5, the results from our reaction probability measurements are presented and compared with values estimated from the results reported by Hanson and Ravishankara⁵ for ternary ($\text{H}_2\text{SO}_4\text{--H}_2\text{O--HCl}$) compositions which closely correspond to our 196, 198 and 201 K solutions. It may be seen that our reaction probabilities for solutions without HNO_3 are slightly lower than those of Hanson and Ravishankara.⁵ Fig. 5 also shows that the incorporation of HNO_3 into the sulfate solutions lowers the reaction probability relative to solutions without HNO_3 only to a small extent, despite the presence of HNO_3 levels as high as 28.3%; the difference is of the order of the experimental uncertainty, although it appears to be statistically significant. Zhang *et al.*⁶ also measured reaction probabilities without HNO_3 at a temperature of 198 K, for one solution containing *ca.* 4% HNO_3 , and found no change in the $\text{ClONO}_2 + \text{HCl}$ reaction probability.

In Fig. 6 the reaction probabilities from Tables 2 and 3 are instead plotted as a function of HCl content. The line in the figure is a least-squares fit; its slope indicates that γ is directly proportional to the square root of the HCl concentration. Hanson and Ravishankara⁵ measured γ over a wide HCl partial pressure (p_{HCl}) range: as expected, at very low p_{HCl} the ClONO_2 decay rate is dominated by reaction (1), and hence is nearly independent of p_{HCl} . For intermediate and high p_{HCl} values γ was found to be proportional to $(p_{\text{HCl}})^{1/2}$ and to p_{HCl} , respectively; Hanson and Ravishankara⁵ interpreted these results in terms of a bulk and a surface component to γ . The measurements of Zhang *et al.*⁶ were carried out at relatively high HCl concentrations, and their data indicate close to linear proportionality between γ and p_{HCl} . Considering the validity of Henry's law for these conditions, the same functional forms should apply to $[\text{HCl}]$: our measurements were carried out at intermediate $[\text{HCl}]$ values, yielding a square-root

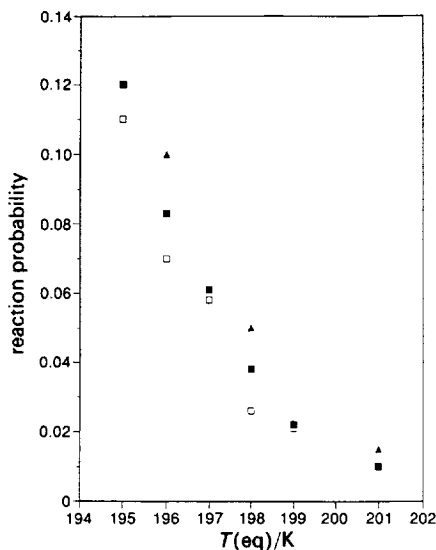


Fig. 5 Reaction probability measurements for HCl + ClONO₂ as a function of atmospheric temperature $T(\text{eq})$, assuming 5 ppm by volume H₂O and 2 ppb by volume HCl at 100 mbar. □, Our data, for 10 ppb by volume HNO₃; ■, our data, assuming no HNO₃; ▲, data estimated from the results of Hanson and Ravishankara⁵ (no HNO₃).

proportionality, in agreement with the results obtained by Hanson and Ravishankara⁵ for similar [HCl] values.

In an attempt to ascertain a dependence of γ on the H₂SO₄ content, we chose a fixed HCl concentration of 2.3×10^{-3} mol dm⁻³ [corresponding to the moderately efficient reaction probability of the 197 K (no HNO₃) solution] and varied the H₂SO₄ content from 40 to 60%. This data is listed in Table 4; it is clear that the reaction probability

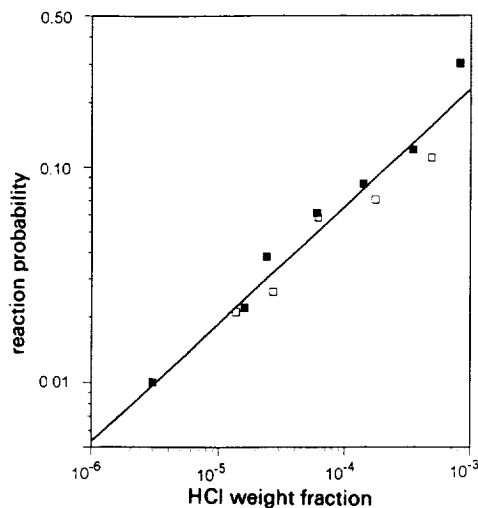


Fig. 6 Reaction probability measurements for HCl + ClONO₂ as a function of HCl weight fraction. □ and ■, experimental data for solutions with and without HNO₃, respectively. The line is a fit through the data; its slope is 0.545.

Table 4 Reaction probabilities for the $\text{H}_2\text{SO}_4\text{--H}_2\text{O--HCl}$ system as a function of temperature and sulfuric acid content, measured at a fixed HCl concentration of $2.3 \times 10^{-3} \text{ mol dm}^{-3}$

$T(\text{exp})/\text{K}$	weight fraction H_2SO_4	reaction probability
203	0.49	0.060
213	0.49	0.061
223	0.49	0.050
233	0.49	0.049
213	0.40	0.057
213	0.45	0.046
213	0.51	0.061
213	0.55	0.059
213	0.60	0.054

does not change significantly over the stratospherically relevant H_2SO_4 content range given in the table. This result, in combination with the laboratory temperature-dependence studies, suggests that the atmospheric temperature (and thus the composition of the aerosols) affects the $\text{ClONO}_2 + \text{HCl}$ reaction probability predominantly through its effect on the HCl solubility. Although the uptake of HNO_3 serves to increase the solubility of HCl, it may be seen (Tables 2 and 3) that reaction probabilities are already very high at the atmospheric temperatures where this effect becomes important.

Conclusions

The Henry's Law solubility constants for HCl reported in this work for the ternary $\text{H}_2\text{SO}_4\text{--H}_2\text{O--HCl}$ and quaternary $\text{H}_2\text{SO}_4\text{--HNO}_3\text{--H}_2\text{O--HCl}$ systems have been shown to agree with the thermodynamic model of Luo *et al.*¹³ for selected atmospherically relevant compositions and temperatures. Furthermore, our new results for the ternary system are in agreement with the previous measurements of Hanson and Ravishankara⁴ and Williams and Golden,¹¹ while our earlier results¹² deviate significantly from these consensus findings.

Our results show that the uptake of substantial levels of nitric acid (as much as 28%) does not appreciably affect the reaction probabilities for the $\text{ClONO}_2 + \text{HCl}$ process on sulfuric acid surfaces. The results also show that the reaction probabilities are not sensitive to temperature for solutions with a given composition. The controlling parameter is the concentration of HCl in the solution, which for a given HCl partial pressure depends in turn on temperature; in the lower stratosphere this concentration increases rapidly below *ca.* 200 K.

Since it is now clear that the $\text{ClONO}_2 + \text{HCl}$ reaction proceeds efficiently on super-cooled liquid sulfuric acid surfaces with compositions relevant to the cold stratosphere, including the possibility of extensive HNO_3 uptake, it is not necessary to invoke the presence of solid PSC particles to explain the high chlorine activation rates associated with large scale ozone depletion. As suggested earlier, the key factor is the stratospheric temperature,⁸ as it approaches the $\text{HNO}_3\text{--H}_2\text{O}$ dew point, the composition of the liquid aerosols changes rapidly,²² with the consequent increase in HCl solubility. If the aerosols are solid, it is the approach to the ice frost point that matters; chlorine activation occurs readily on the ice-like surfaces. We note, however, that a change in phase for the stratospheric aerosols might have other important consequences: the surface area available for reaction can change with freezing and, more importantly, the mechanism for efficient denitrification might involve nucleation of a small fraction of the liquid particles; the solid ones would then selectively grow and fall out of the stratosphere.

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